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(12) Patent: (11) CA 911136

(54) LOW TEMPERATURE WATER GAS SHIFT REACTION

(54)

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(45) Issued on: Oct. 3, 1972

(22) Filed on:

(43) Laid open on:

(52) Canadian Class (CPC): 23/29 23/316 48/33 252/89

(51) International Class (IPC): N/A

Patent Cooperation Treaty (PCT): No

(30) Application priority data: None

Availability of licence: N/A

Language of filing: Unknown

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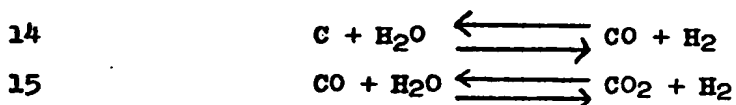
ABSTRACT:

## ABSTRACT OF THE DISCLOSURE

Hydrogen is produced by reacting carbon monoxide with steam at a temperature of at least 200°F. in the presence of (1) at least one alkali metal compound derived from acids having ionization constants below  $1 \times 10^{-3}$  and (2) a metallic hydrogenation-dehydrogenation material. The ratio of metal component to the alkali metal compound, calculated on the basis of the oxides thereof, ranges from 0.0001 to about 10 parts by weight per part by weight of the alkali metal compound. The alkali metal compound may be impregnated on the hydrogenation-dehydrogenation component or may be mixed with or used in the presence of the metal component. A preferred catalyst combination is a potassium compound, such as potassium carbonate, mixed with cobalt-molybdenum on an alumina support.

1           This invention relates generally to a process for  
2 producing hydrogen by reacting carbon monoxide with steam at  
3 elevated temperatures in the presence of at least one alkali  
4 metal compound and at least one metal hydrogenation-dehydro-  
5 genation component. More particularly, the invention relates  
6 to a process for producing hydrogen by reacting carbon monoxide  
7 with steam at a temperature of at least 200°F. in the presence  
8 of an alkali metal compound derived from an acid having an  
9 ionization constant less than  $1 \times 10^{-3}$  with at least one metal  
10 hydrogenation-dehydrogenation material.

11           The present invention relates to the preparation of  
12 hydrogen from carbonaceous materials in accordance with the  
13 equations:



16           It is well known to prepare hydrogen by reacting  
17 carbonaceous materials, such as hydrocarbons with steam at  
18 elevated temperatures of 1200° - 1400°F. or coal or coke with  
19 steam at temperatures up to 2500°F. and then to react the  
20 resulting mixture of CO and H<sub>2</sub> with more steam at lower tem-  
21 peratures, for example, at 800° - 900°F. in the presence of  
22 suitable catalysts to convert the carbon monoxide produced in  
23 the first stage to carbon dioxide and additional hydrogen. The  
24 second step, known as the water gas shift reaction, is limited  
25 by equilibrium considerations and complete conversion of CO to  
26 CO<sub>2</sub> is not realized. However, the concentration of CO in the  
27 product when equilibrium is reached is highly dependent on the  
28 temperature. Consequently conversions can be increased by  
29 either removing the carbon dioxide and again contacting the CO  
30 and steam with the catalyst in the same or subsequent stages  
31 or by lowering the temperature.



The effect of temperature on the equilibrium constant

$K = \frac{(CO_2)(H_2)}{(CO)(H_2O)}$  is shown in the following table.

	°F.	K	Concentration of CO at Equilibrium (dry basis) Feed*	
			A	B
8	900	5.61		
9	800	9.03	5.19	
10	700	15.89	3.30	1.12
11	600	31.44	1.77	0.56
12	500	72.75		
13	400	206.8	0.29	

\* A - 50% of a 1/1 H<sub>2</sub>/CO mixture + 50% H<sub>2</sub>O (steam)  
 B - 30% of a 1/1 H<sub>2</sub>/CO mixture + 70% H<sub>2</sub>O (steam)

It is thus evident that less CO will remain unconverted and costly methods of operation will be avoided by operating at as low temperatures as possible, e.g., 300° - 700°F., preferably 400° - 600°F. Such low temperatures can be employed by the use of a catalyst consisting of copper deposited on zinc oxide. Unfortunately, however, this catalyst will not tolerate even traces of sulfur in the feed. Since coal and coke and heavy hydrocarbon feeds suitable for conversion to hydrogen contain appreciable amounts of sulfur, e.g., up to 5 to 10 wt. %, which is converted to hydrogen sulfide and even some small amounts of carbon disulfide and carbonyl sulfide, these feeds are precluded from use with the Cu-ZnO catalyst, and are limited to shift temperatures of 750° - 900°F. using a sulfur resistant catalyst such as Fe<sub>2</sub>O<sub>3</sub> promoted with Cr<sub>2</sub>O<sub>3</sub>.

It has now been found that gas mixtures containing carbon monoxide contaminated with relatively large amounts of sulfur can be converted to hydrogen economically by reaction with steam at a temperature of at least 200°F. in the presence of (1) at least one alkali metal compound, said compound being derived from an acid having an ionization constant less than about  $1 \times 10^{-3}$ , and (2) a hydrogenation-dehydrogenation component. The alkali metal compound (Group IA compound) and the

1 hydrogenation-dehydrogenation component may be supported on a  
2 carrier together or separately. In addition, the alkali metal  
3 compound may be impregnated on the hydrogenation-dehydrogena-  
4 tion component. Suitable hydrogenation-dehydrogenation com-  
5 ponents include: (a) Group VIII noble metals, in particular,  
6 rhodium, ruthenium, palladium, osmium, iridium and platinum  
7 metals and compounds thereof; (b) non-noble metal materials  
8 including vanadium, molybdenum, cobalt, tungsten metals and  
9 compounds thereof including mixtures thereof, in particular,  
10 the oxides and sulfides; and (c) mixtures of one or more vana-  
11 dium, molybdenum, cobalt and tungsten metals or compounds  
12 (oxides or sulfides) with one or more nickel, iron or chromium  
13 materials, e.g., nickel, iron or chromium metals or compounds  
14 (oxides or sulfides) thereof.

15         At least a portion of the non-noble catalyst species  
16 (categories (b) and (c) above) should exist in a sulfided form.  
17 Such catalysts are particularly suitable for use with feeds  
18 containing sulfur. However, these catalyst compositions may  
19 also be used with sulfur-free feeds. When sulfur-containing  
20 feeds are used, the non-noble metal catalyst may be sulfided  
21 in situ by passing the feed over the oxide or other compound  
22 which is then converted at least partially to a sulfide. The  
23 noble metal containing catalysts are at least partially deact-  
24 ivated through contact with sulfur. Hence, these catalysts  
25 should be used with substantially sulfur-free feedstocks.

26         The ratio of hydrogenation-dehydrogenation component  
27 to alkali metal compound is a critical feature of the instant  
28 invention. Maximum catalyst activity is encountered when the  
29 ratio of metal component to alkali metal compound varies from  
30 about 0.001 to about 10 parts by weight per part by weight of  
31 alkali metal compound, the weight ratios being calculated on  
32 the basis of the oxides of each constituent. When noble metal

1 based catalysts are used, the ratio of metal component to alk-  
2 ali metal compound, calculated on the basis of the oxides  
3 thereof, desirably varies from about 0.0001:1 to about 10:1.  
4 For purposes of calculating weight ratios, the metals are  
5 assumed to exist in only the following oxide forms:  $\text{CoO}$ ,  $\text{MoO}_3$ ,  
6  $\text{WO}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{NiO}$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{RuO}_3$ ,  $\text{RhO}_2$ ,  $\text{PdO}$ ,  $\text{OsO}_3$ ,  $\text{Ir}_2\text{O}_3$  and  
7  $\text{PtO}_2$ .

8 The figure is a plot of the relative activities of  
9 various shift catalysts as a function of the weight ratio of  
10 the hydrogenation-dehydrogenation component to the alkali metal  
11 component of the catalyst.

12 The first stage reaction in the preparation of hydro-  
13 gen consists in reacting coal, coke or heavy feeds at  $1000^\circ$ -  
14  $2500^\circ\text{F}$ . with steam with or without the presence of hydrogen or  
15 the reaction of natural gas or other hydrocarbons with steam  
16 in the presence of reformer catalysts containing nickel, cobalt,  
17 etc. promoted with magnesia, alumina, thoria and similar  
18 oxides and supported, if desired, on an inert base at tempera-  
19 tures of  $1200^\circ$  -  $1600^\circ\text{F}$ . Hydrogen, carbon dioxide and carbon  
20 monoxide are obtained with a high ratio of  $\text{CO}$  to  $\text{CO}_2$ .

21 In accordance with my earlier findings, the second  
22 stage, or shift reaction, in which the carbon monoxide formed  
23 in the first stage is reacted with more steam at  $300^\circ$  -  $700^\circ\text{F}$ .,  
24 preferably  $400^\circ$  -  $600^\circ\text{F}$ ., may be carried out in the presence  
25 of a cesium compound, derived from an acid with a  $\text{pK}_a$  less than  
26  $1 \times 10^{-3}$ , supported on a carrier. These catalysts are affected  
27 to some extent by sulfur but are sufficiently resistant to sul-  
28 fur so that acceptable conversion of  $\text{CO}$  to  $\text{CO}_2$  can be obtained.

29 The present invention makes it possible not only to  
30 overcome the effect of sulfur on the alkali metal compounds but  
31 also enables substantially complete conversion of carbon mon-  
32 oxide to carbon dioxide to be achieved in one step at low

1 temperatures, an accomplishment which has heretofore been im-  
2 possible in the presence of sulfur. These results are obtained  
3 in accordance with the present invention by carrying out the  
4 reaction in the additional presence of from about 0.001 to 10  
5 parts by weight of a non-noble metal hydrogenation-dehydrogena-  
6 tion catalyst component per weight of alkali metal (based upon  
7 the weight of the oxides thereof) without reference to any  
8 support which may be used. The use of these catalysts in con-  
9 junction with the alkali metal salt enables more complete con-  
10 version of the carbon monoxide to carbon dioxide even in the  
11 presence of sulfur and thus affords vast economic savings since  
12 a costly step of removing the carbon dioxide is avoided.

13         While it is not intended to be limited by any theory  
14 concerning the mechanism of the reaction, it is believed that  
15 the alkali metal component in the presence of water vapor  
16 (steam) exists as a liquid phase in contact with the surface  
17 of the hydrogenation-dehydrogenation component. It is believed  
18 that the aqueous alkali metal phase converts the carbon mon-  
19 oxide to formate and the hydrogenation-dehydrogenation catalyst  
20 surface converts the formate into  $\text{CO}_2$  and  $\text{H}_2$ . Thus the inter-  
21 action between the two types of catalysts brings about a vast  
22 synergistic effect on catalytic activity. Nevertheless, in  
23 the preferred embodiment of this invention, the reaction con-  
24 ditions are such that the process reactants, specifically the  
25 process steam, are present in the reaction zone in predominantly  
26 the vapor phase. If liquid phase conditions exist, the propor-  
27 tion of the steam present in the liquid phase is relatively  
28 small compared to the total amount of steam employed in the  
29 process.

30         Suitable alkali metal components include the carbonate,  
31 bicarbonate, biphosphate, sulfide, hydrosulfide, silicate, bi-  
32 sulfite, aluminate, hydroxide, acetate, tungstate, etc. of



1 sodium, potassium, lithium, rubidium and cesium. In addition,  
2 the alkali metal salts of organic acids such as acetate are  
3 equally suitable. Actually the alkali salt of any acid which  
4 has an ionization constant of less than  $1 \times 10^{-3}$  may be used.  
5 The potassium and cesium salts, in particular potassium and  
6 cesium carbonate, are most preferred.

7         It has been discovered that at least a portion of the  
8 weak acid alkali metal salts are converted to the correspond-  
9 ing alkali metal carbonate during the course of the shift re-  
10 action. Additionally, salts of relatively unstable strong  
11 acids, such as nitric acid, are also converted, at least par-  
12 tially, to the carbonate. Hence, in most instances, the ul-  
13 timate catalyst specie is believed to be the alkali metal car-  
14 bonate. Therefore, the alkali metal catalyst constituent may  
15 be any material that is at least partially converted to the  
16 alkali carbonate during the course of the shift reaction.

17         The hydrogenation-dehydrogenation component of the  
18 catalyst system may be noble metal materials, in particular,  
19 ruthenium, palladium, osmium and platinum metals. Non-noble  
20 metal materials, in particular sulfided metals, are highly  
21 effective catalysts. Vanadium, molybdenum, cobalt, tungsten  
22 and mixtures thereof, alone or in combination with nickel, iron  
23 or chromium compounds, are the preferred non-noble catalyst  
24 compositions. Examples of useful heavy metal catalyst com-  
25 ponents include molybdenum-chromium, tungsten-chromium, cobalt-  
26 nickel, cobalt-iron, molybdenum-tungsten, vanadium-tungsten,  
27 platinum-tungsten, iridium-cobalt, rhodium-cobalt, vanadium-  
28 cobalt, molybdenum, cobalt-iron, nickel-tungsten, vanadium,  
29 platinum, palladium, cobalt-nickel-molybdenum, cobalt-iron-  
30 molybdenum, etc.

31         If the above non-noble metals are used with sulfur-  
32 containing feeds, they may be initially employed in the form

1 of the oxide or other compound easily sulfided. These com-  
2 pounds are then sulfided in situ during the passage of the  
3 sulfur-containing feed over them. Cesium or potassium carbon-  
4 ate or acetate combined with cobalt-molybdenum oxides and/or  
5 sulfides is a particularly effective catalyst combination.  
6 Hereinafter, the non-noble catalysts will be referred to as the  
7 metal without reference to how it is combined since the actual  
8 composition, prior to shift reaction, is, for example, cobalt  
9 oxide-molybdenum oxide-aluminum oxide and the like. Under the  
10 reaction conditions the non-noble metal based catalyst usually  
11 exists in a partially reduced and sulfided state which is  
12 difficult to define stoichiometrically and thus a description  
13 using the active metallic elements is as accurate as any. It is  
14 believed that the active noble metal catalyst specie is the  
15 metal itself. Typically, noble metal containing catalysts are  
16 introduced into the reactor in the oxide form. The noble metal  
17 oxide is thereafter converted to the active catalyst species  
18 during the course of the shift reaction.

19       The catalytically active metal components may be used  
20 either supported or unsupported and in the former case the  
21 nature of the carrier is not critical. Suitable carriers in-  
22 clude alumina having an extremely broad range of surface areas,  
23 such as gamma and alpha aluminas. Other suitable support mate-  
24 rials include silica, silica-alumina, e.g., silica-alumina  
25 cogel cracking catalysts; zeolites such as faujasite, erionite,  
26 and the like; activated carbon, coconut charcoal, magnesia,  
27 boria, thorina, titania, zirconia and the like. Particularly  
28 suitable gamma and alpha-alumina catalyst supports are avail-  
29 able commercially. Such supports may be prepared by a variety  
30 of methods. For example, they may be prepared by hydrolyzing  
31 an aluminum alcoholate which may have been prepared in accord-  
32 ance with the disclosures of U.S. Patent 2,636,865. They may

1 also be prepared by precipitating a hydrous alumina from an  
2 aqueous solution of an aluminum salt, preferably  $\text{AlCl}_3$ . A third  
3 method of preparation comprises dissolving metallic aluminum  
4 in weakly acidified water, preferably acidified with an organic  
5 acid, such as acetic acid, in the presence of mercury or com-  
6 pound thereof, and thereafter gelling the alumina sol thus  
7 formed. The hydrous alumina prepared by any of the foregoing  
8 procedures is subsequently dried and calcined at temperatures  
9 between  $600^\circ$  and  $1200^\circ\text{F.}$ , preferably between  $900^\circ$  and  $1000^\circ\text{F.}$

10 The extent of the surface area of the support material  
11 employed is believed to be a factor in the performance of the  
12 total catalyst system. Desirably, the catalyst support has a  
13 relatively low surface area, e.g., less than about  $50\text{-}100\text{ m}^2/\text{gram}$ ,  
14 as determined by the BET Method. Low surface area supports,  
15 such as alpha alumina having a surface area of less than about  
16  $5\text{ - }20\text{ m}^2/\text{gram}$  (BET Method), are effective catalyst carriers,  
17 in particular, for noble metal-containing catalysts.

18 The catalyst components can be incorporated on the  
19 support in any conventional manner. Preferably, the hydrogena-  
20 tion-dehydrogenation components are placed on the support first  
21 and this combination is then calcined, e.g., at  $1000^\circ\text{ - }1200^\circ\text{F.}$ ,  
22 to convert the metals to the stable oxide forms. Then the alk-  
23 ali metal, e.g., cesium or potassium carbonate, is impregnated  
24 onto the support using aqueous or alcoholic media and the  
25 catalyst simply dried. The impregnation operation can be car-  
26 ried out before the remaining catalyst is introduced into the  
27 reactor or after the remaining catalyst constituents are in  
28 place within the reaction zone. In general, the carrier mate-  
29 rial is impregnated with a solution containing the desired com-  
30 pound. The finished catalyst is then sulfided in a known man-  
31 ner, e.g., by passing over the catalyst a mixture of hydrogen  
32 and hydrogen sulfide, carbon disulfide, butyl mercaptan and

1 the like. However, it may be sulfided in situ as described  
2 above. Alternatively, sulfur can be placed on the catalyst by  
3 introducing the alkali compound as the alkali sulfide.

4 Alternatively, the various components may be mixed  
5 by mechanical means, such as by dry mixing. Good catalysts  
6 can be obtained by fine milling of a cobalt-molybdenum catalyst  
7 supported on alumina and mixing the powder obtained with a pow-  
8 dered alkali metal compound such as cesium carbonate. The re-  
9 sultant mixture, after the addition of a lubricant such as  
10 stearic acid or graphite, is compressed into pellets which can  
11 be calcined and sulfided.

12 The hydrogenation-dehydrogenation component is gen-  
13 erally used in amounts varying from about 0.0001 to about 5 -  
14 10 parts by weight based on the alkali metal compound. In the  
15 case of non-noble metal catalysts, the metal constituent/alkali  
16 metal compound weight ratio preferably varies from about 0.01  
17 to about 5.0 parts by weight of hydrogenation-dehydrogenation  
18 material and, most preferably, from 0.1 to 3.0 parts by weight  
19 of non-noble metal catalyst per part by weight of alkali metal  
20 compound, exclusive of any carrier which might be used to sup-  
21 port either or both components. All components are calculated  
22 on the basis of the oxide thereof.

23 When a carrier is used the ratio of catalyst compo-  
24 nents (metal material and alkali compound) to carrier is not  
25 critical but may range from about 90 wt. % to about 0.5 wt. %,  
26 however, it has been found most desirable to use amounts of  
27 from about 50 to about 1 wt. %, all based on total catalyst  
28 including the carrier. Hydrogenation-dehydrogenation catalysts  
29 which have been found particularly effective contain cobalt  
30 oxide and molybdenum oxide on gamma alumina prior to sulfiding.  
31 Particularly suitable ranges of catalyst components are from  
32 about 0.1 to about 10 wt. % cobalt oxide and from about 1 to

1 about 25 wt. % molybdenum oxide. Most suitable are hydrogenation-dehydrogenation components present in an amount of from  
2 1 to about 5 wt. % cobalt oxide and from 5 to about 15 wt. %  
3 molybdenum oxide. This catalyst component can then be impregnated with about 5 to about 80 wt. % of alkali metal compound  
4 and sulfided to make the final catalyst. Alternatively, the  
5 alkali metal compound may be itself supported independently of  
6 the hydrogenation-dehydrogenation component, both of which may  
7 be mixed together and then sulfided to make the catalyst  
8 composition.

9 The shift process is preferably carried out continuously. The gaseous hourly space velocity can vary within wide  
10 limits. Gaseous hourly space velocities of at least 300 volumes of feed per volume of supported catalyst per hour (V/V/Hr),  
11 preferably space velocities between about 300 and 30,000  
12 (V/V/Hr), measured on the basis of dry gas under standard conditions are particularly suitable for most applications. The  
13 process may be carried out at higher gaseous hourly space  
14 velocities if desired.

15 Referring now more specifically to the shift process,  
16 except for the low temperature, with its favorable effect on  
17 reaction equilibrium, resulting from the practice of this invention, water gas shift reactions are well known. Carbon monoxide  
18 or a gas containing 0.1% or more carbon monoxide by volume, and  
19 steam in an amount of 1-100 volumes per volume of carbon monoxide, are introduced into a shift converter and passed over  
20 the alkali metal and hydrogenation-dehydrogenation catalyst at  
21 a temperature between 200° and 700°F. The pressure is preferably in the range of 200 to 1500 pounds per square inch gauge  
22 (psig), although it may vary from atmospheric to 3000 psig or  
23 more. However, the exact pressure and temperature conditions

1 must be maintained above the dew point of the steam in the mix-  
2 ture. The process is particularly effective when the feed con-  
3 tains sulfur. In fact, the presence of sulfur in the feed  
4 actually results in increased conversions in many cases. If  
5 necessary, the catalyst may be regenerated by oxidation and  
6 resulfiding.

7           The use of the catalyst system of this invention leads  
8 to an extremely high heat release. Heat control may therefore  
9 be an important consideration in designing process equipment.  
10 Heat problems may be avoided with the use of a fluidized process  
11 in place of the fixed bed process normally used for shift  
12 reaction. If a fixed bed process is used, the high heat re-  
13 lease might be accommodated by the use of an inert diluent or  
14 by pseudo staging of the catalyst beds by diluting the catalyst  
15 along the length of the catalyst beds.

16           Typical results of operations in accordance with the  
17 process of this invention are given in the following examples.  
18 It will be evident that the examples are merely illustrative of  
19 the invention and no undue limitation is imposed thereby. In  
20 all cases herein the analyses of the hydrogenation-dehydrogena-  
21 tion component are calculated on the basis of the metals ex-  
22 pressed as the oxides and the alkali metal component expressed  
23 as the oxides.

24 EXAMPLE 1

25           A gas mixture consisting of approximately 46% hydro-  
26 gen, 53% carbon monoxide and about 1%  $H_2S$  was used as feed.  
27 This gas feed was passed through a reactor containing a cata-  
28 lyst at 550 psig at such a rate as to maintain an exit dry gas  
29 product rate of 2700 V/V/Hr. measured at room temperature and  
30 1 atmosphere of pressure and together with the feed gas was fed  
31 steam in the mole ratio of one mole per mole of dry product gas.  
32 The catalyst consisted of cobalt-molybdenum dispersed on gamma

1 alumina having a surface area of 200-400 M<sup>2</sup>/g., the cobalt con-  
 2 tent corresponding to 3.5 wt. % of CoO and the molybdenum con-  
 3 tent corresponding to 13 wt. % MoO<sub>3</sub> and which was impregnated  
 4 with 44 - 48 wt. % of cesium acetate in an aqueous solution  
 5 ( $1.7 \times 10^{-3}$  moles per cc catalyst volume) and dried at about  
 6 150°C. The catalyst was then sulfided in situ by passing the  
 7 feed over the catalyst for about an hour at a temperature of  
 8 625°F. The following results were obtained.

TABLE I

Run No.	1	2	3
Metals	CoMo	CoMo	None
Alkali metal compound	Cs Acetate	Cs Acetate	Cs Acetate
$\gamma$ -alumina support	Type A	Type B	Type B
% CO in Product			
Temp. °F.	Pressure psig		
625	550	1.16	1.17
525	550	0.53	0.54
475	550	0.43	
425	550	0.32	0.40
425	200	0.31	0.23
350	200	20.57	
350	0	45.54	41.35

24 The above data show that a mixture of cesium acetate  
 25 and cobalt-molybdenum is an extremely effective and efficient  
 26 catalyst for catalyzing the water gas shift reaction down to  
 27 temperatures as low as 350°F. This compares very favorably  
 28 with the results obtained with cesium acetate alone under the  
 29 same conditions where 48.61% of carbon monoxide remained in  
 30 the product at 625°F. Feed gas and product gas analyses are  
 31 expressed as mol. %.

EXAMPLE 2

33 The experiment of Example 1 was repeated except that  
 34 the cobalt and molybdenum were used separately. The results  
 35 are shown in Table II.

TABLE II

Run No.	4	5
Metals	Co (4.4 wt.% CoO)	Mo (11 wt.% MoO <sub>3</sub> )
Alkali	Cs Acetate	Cs Acetate

% CO in Product

Temp. °F.	Pressure psig		
625	550	4.10	1.53
525	550	32.83	11.56

These two examples illustrate the enhanced effectiveness of the cobalt-molybdenum combination in contrast to each component alone, even though all of these systems are effective catalysts in the invention.

EXAMPLE 3

The experiment of Example 1 was repeated showing the effect of varying the alkali metal component when using cobalt-molybdenum. The results are reported in Table III.

TABLE III

Run No.	6	7
Metals	CoMo	CoMo
Alkali	K Acetate	Cs <sub>2</sub> CO <sub>3</sub>
	(1.7 x 10 <sup>-3</sup> moles/cc catalyst)	(8.7 x 10 <sup>-4</sup> moles/cc catalyst)

% CO in Product

Temp. °F.	Pressure psig		
625	550	1.19	1.28
525	550		0.59
475	550		
425	550	0.39	0.37
425	200	0.77	0.35
350	200		
350	0		43.67

The above data show that potassium acetate is substantially as effective as cesium acetate down to temperatures as low as 425°F. and that cesium carbonate is just as effective.

EXAMPLE 4

The experiment of Example 1 was again repeated to show the effect of changing the non-noble metal constituent. The results are shown in Table IV.



TABLE IV

Run No.	9	10
Metals	FeMo	NiMo
Alkali	Cs Acetate	Cs Acetate
% CO in Product		
Temp. °F.	Pressure psig	
625	550	1.15
525	550	11.32
475	550	1.26
425	550	0.87
		35.07

The above data show that nickel-molybdenum and iron-molybdenum are also effective catalyst in the carbon monoxide reaction.

## EXAMPLE 5

The experiment of Example 1 was again repeated to show the effect of different non-noble metal catalyst constituents. The data are reported in Table V.

TABLE V

Run No.	12	13	14
Metals	CoV	CoCr	CoW
Alkali	Cs Acetate	Cs Acetate	Cs Acetate
% CO in Product			
Temp. °F.	Pressure psig		
625	550	7.18	17.24
525	550	46.08	22.93
			42.41

The above data show the effectiveness of vanadium, chromium, and tungsten as catalysts when used with cobalt.

## EXAMPLE 6

The experiment of Example 1 was repeated to show the effects of using the cobalt-molybdenum in the absence of the alkali metal.

TABLE VI

Run No.	15
Metals	CoMo
Alkali	None

<u>% CO in Product</u>			
	<u>Temp.</u>	<u>Pressure</u>	
	<u>°F.</u>	<u>psig</u>	
4	625	550	1.08
5	525	550	
6	475	550	
7	425	550	38.71
8	425	200	47.19

9           The above table shows that the cobalt molybdenum  
10 component alone is only one hundredth as effective (based on  
11 first order reaction rates) as when it is used with cesium  
12 acetate or carbonate. (See Run 1, Example 1 and Run 7, Example  
13 3).

#### 14 EXAMPLE 7

15           Run 1 of Example 1 was repeated to determine the  
16 effect of sulfiding on the effectiveness of the catalyst on  
17 feeds containing sulfur as well as on sulfur-free feeds. The  
18 following results were obtained at 625°F.

<u>TABLE VII</u>				
20 Run No.	16	17	18	
21 Catalyst	Unulfided	Sulfided	Presulfided	
22		in situ		
23 Feed				
24 H <sub>2</sub>	45.9	46.44	45.9	
25 CO	54.1	52.51	54.1	
26 H <sub>2</sub> S	0	1.4	0	
27 Product				
28 CO	17.32	1.19	1.18	
29 CO Conversion %	57.9	96.5	96.7	

30           The above data show that the sulfided catalyst whe-  
31 ther sulfided in situ (Run No. 17) or presulfided with no sul-  
32 fur in the feed (Run No. 18) gives equilibrium conversions of  
33 carbon monoxide while the unsulfided catalyst with no sulfur  
34 in the feed (Run No. 16) gives much poorer conversion.

#### 35 EXAMPLE 8

36           The conditions of Example 1 were repeated with var-  
37 ious catalysts to show the effect of varying the type of  
38 support, using a low surface area alpha Al<sub>2</sub>O<sub>3</sub>, faujasite, and  
39 carbon as compared to the high surface area gamma alumina of  
40 Run 2 (Example 1).

TABLE VIII

Run No.	2	19	20	21
Support	$\gamma$ - $\text{Al}_2\text{O}_3$	Faujasite	$\alpha$ - $\text{Al}_2\text{O}_3$	Activated Carbon
Metals	CoMo (3.5 % CoO 13% $\text{MoO}_3$ )	CoMo (3.7% CoO 13.8% $\text{MoO}_3$ )	CoMo (1.6% CoO 6.0% $\text{MoO}_3$ )	Mo (12% $\text{MoO}_3$ )
Alkali	Cs Acetate	Cs Acetate	Cs Acetate	Cs Acetate
Temp. °F.	Pressure psig		% CO in Product	
625	550	1.17	1.15	1.18
525	550	0.54	0.62	0.51
475	550			( $<1.03$ )
425	550	0.40		
425	200	0.23	32.3	
350	200			
350	0	41.35		

## EXAMPLE 9

When a catalyst containing sodium carbonate and a cobalt-molybdenum on alumina hydrogenation-dehydrogenation catalyst is used according to Example 1 at 600°F. the CO is substantially completely converted to the thermodynamic equilibrium concentration of  $\text{CO}_2$ .

## EXAMPLE 10

A gas mixture consisting of approximately 46% hydrogen, 53% carbon monoxide and about 1%  $\text{H}_2\text{S}$  was used as a feed gas. This gas feed was passed through a catalyst containing reactor at 550 psig at such a rate as to maintain an exit dry gas product rate of 2700 V/V/Hr. under conditions of room temperature and 1 atmosphere of pressure, and together with the feed gas was fed steam in the mole ratio of 1 mole per mole of dry product gas. The cobalt-molybdenum used in this experiment was prepared in the same manner and had the same percentage composition as that used in Example 1. This cobalt-molybdenum component was impregnated with an aqueous solution of potassium carbonate ( $\text{K}_2\text{CO}_3$ ) in an amount equivalent to  $8.7 \times 10^{-4}$  moles per cc catalyst volume, and was dried at about 150°C. Based on total catalyst composition there was 13.6 weight percent

1 potassium carbonate. The catalyst was then sulfided by means  
2 of a standard method. The following results were obtained.

3 TABLE IX

4 5 6	Reaction Temp., °F.	Reaction Pressure (psig)	% CO in Product	
			Found	Thermodynamic Equilibrium
7	550	550	0.64	0.63
8	425	200	0.20	0.22

9 The above data show the clear advantage of employing  
10 the potassium carbonate on the hydrogenation-dehydrogenation  
11 component.

12 EXAMPLE 11

13 A series of tests were conducted to demonstrate the  
14 criticality of employing an alkali metal material as a shift  
15 catalyst constituent as opposed to utilizing related alkaline  
16 earth metal materials. In each of the tests the alkali or  
17 alkaline earth metal composition was impregnated upon a base  
18 catalyst composed of 3.5 wt. % cobaltous oxide and 13.0 wt. %  
19 molybdenum oxide on gamma-alumina. The base catalyst was from  
20 20-40 U.S. standard screen mesh size. Thirty cubic centimeters  
21 of each of the catalyst materials were charged into a small  
22 cylindrical reactor having a 10:1 length to diameter ratio. The  
23 reactor was positioned within a sand bath.

24 In each of the tests a carbon dioxide-free gas mix-  
25 ture composed of approximately 52 volume % carbon monoxide, 47  
26 volume % hydrogen, and about 1 volume % hydrogen sulfide was  
27 employed as the process reagent. All the tests were conducted  
28 at a temperature of about 425°F. at a reaction zone pressure  
29 of about 200 psig. The gas reagent was passed through the re-  
30 actor at a rate such as to maintain an exit dry gas product  
31 rate of 2700 volumes of gas/volume of catalyst/hour measured  
32 at room temperature and atmospheric pressure. Steam was intro-  
33 duced into the shift reactor in a mole ratio of 1 mole of steam

1 per mole of dry product gas.

2 After charging the catalyst to the reactor, the cata-  
 3 lyst was sulfided by passing the feed gas mixture over the  
 4 catalyst for about 110 minutes at 250°F. and atmospheric pres-  
 5 sure. Thereafter the catalyst bed was gradually heated from  
 6 250°F. to 625°F. over a period of 135 minutes while continuously  
 7 being contacted with feed gas mixture at atmospheric pressure.  
 8 The 625° temperature level was then maintained for an additional  
 9 130 minutes while continuing to contact the catalyst with the  
 10 gas mixture at atmospheric pressure. All of these operations  
 11 were conducted at a gas rate of about 1.33 liters per minute.  
 12 Thereafter, the reaction zone pressure was raised to 75 psig  
 13 and feed gas introduced into the system at 625°F. for 30 minutes  
 14 at a gas rate of about 2.66 liters per minute. The reactor was  
 15 then pressurized to 550 psig and the feed gas introduced at a  
 16 rate of 2.66 liters per minute for an additional 60 minutes  
 17 while the reaction zone was maintained at 625°F. Finally,  
 18 steam with feed gas was passed through the system at 625°F. and  
 19 then at 525°F.

20 Following this sulfiding procedure, the reactor was  
 21 brought to the process conditions enumerated above. The effec-  
 22 tiveness of each catalyst was ascertained by analyzing the pro-  
 23 cess effluent for CO conversion. Two tests were conducted for  
 24 each catalyst over duplicate time periods of about 20 to 45  
 25 minutes each. The results of the tests are set forth in Table  
 26 X below.

27 TABLE X

28 Alkali or Alkaline		29	% CO
Earth Component	Amount Component Used		Conversion(d)
30 K <sub>2</sub> CO <sub>3</sub>	4.79 grams/40 cc of base		99.4(b)
31	catalyst volume (a)		
32 None			47.1
33 Mg(OOCH) <sub>2</sub>	5.26 grams/40 grams of base		48.7
34	catalyst(c)		

1	Sr(OH) <sub>2</sub>	4.20 grams/40 cc base	16.6
2		catalyst volume	
3	Ba(OH) <sub>2</sub> ·8H <sub>2</sub> O	16.4 grams/40 cc base	26.9
4		catalyst volume	
5	(a) Corresponds to about 15-16 wt. % K <sub>2</sub> CO <sub>3</sub> . Forty cubic		
6	centimeters of absolutely dry base catalyst weighs		
7	about 26.95 grams.		
8	(b) Thermodynamic equilibrium.		
9	(c) Corresponds to about 52.5 cc of base catalyst.		
10	(d) Approximate average values.		

11           The data presented in Table X clearly demonstrates  
 12 that alkaline earth metal compositions are substantially less  
 13 effective catalyst components as compared with potassium car-  
 14 bonate. In fact, the strontium and barium catalyst materials  
 15 were substantially ineffective as they served to diminish the  
 16 catalyst activity associated with the supported cobalt and  
 17 molybdenum materials when used without an alkali metal co-  
 18 catalyst.

#### 19 EXAMPLE 12

20           Tests were conducted to ascertain the effect of add-  
 21 ing an alkali metal compound, specifically potassium carbonate,  
 22 to commercially employed Girdler G-3B iron-chromia shift  
 23 catalysts. The iron-chromia catalyst was not analyzed but was  
 24 believed to be made up of about 15 wt. % chromia and the bal-  
 25 ance iron oxide. One portion of the catalyst was impregnated  
 26 with potassium carbonate in the amount of 4.79 grams of potas-  
 27 sium carbonate per 40 cc's of iron-chromia base catalyst. The  
 28 catalyst materials were then tested for their ability to con-  
 29 vert carbon monoxide. The apparatus described in Example 11  
 30 was used in the tests.

31           In the tests, which were conducted at 625°F. and 550  
 32 psig pressure, the catalysts were presulfided using the pro-  
 33 cedure of Example 11 and were contacted thereafter with a feed  
 34 gas mixture comprising 1.09 volume % hydrogen sulfide, 45.12

1 volume % hydrogen, and 52.3 volume % carbon monoxide. The gas  
2 was introduced into the reaction zone at a rate sufficient to  
3 maintain an exit dry gas product rate of 1.33 liters per min-  
4 ute at room temperature. This corresponds to about 1.21 liters  
5 per minute at standard conditions. About 1.00 cubic centi-  
6 meter of water was introduced into the reaction zone as high  
7 temperature steam per minute.

8         The conventional iron-chromia catalyst and the potas-  
9 sium carbonate promoted iron-chromia catalyst were each sub-  
10 jected to three separate test runs totaling two hours duration.  
11 The conventional iron-chromia catalyst, that was not promoted  
12 with any carbonate material, served to convert, based on an  
13 average of the three runs, about 67.3 mole % of the carbon  
14 monoxide fed to the reactor. In contrast, the iron-chromia  
15 catalyst containing the potassium carbonate promoter served to  
16 convert only 42.2 mole % of the carbon monoxide fed to the  
17 reactor based upon an average of the three runs conducted with  
18 the catalyst. This result was most surprising since, as  
19 demonstrated in previous examples, closely related metal com-  
20 positions such as cobalt-molybdenum, cobalt-vanadium, cobalt-  
21 chromium, iron-molybdenum, nickel-molybdenum are effective  
22 shift conversion catalysts at the temperatures and pressures  
23 employed in this example when used in conjunction with an  
24 alkali metal composition.

25 EXAMPLE 13

26         A series of tests were conducted to demonstrate the  
27 criticality of the ratio of hydrogenation-dehydrogenation com-  
28 ponent to alkali metal compound present in the catalyst system  
29 of the present invention. In the tests, the cobalt oxide-  
30 molybdenum oxide gamma-alumina base catalyst described in  
31 Example 11 was impregnated with varying amounts of potassium  
32 carbonate or cesium carbonate and the activity of the catalyst

1 tested under various conditions of temperature and pressure  
2 with feed streams containing carbon monoxide, hydrogen and  
3 hydrogen sulfide. Additionally, the activity of commercial  
4 iron-chromia catalysts was determined under similar conditions.  
5 Finally, comparisons were made with respect to catalysts that  
6 were presulfided prior to use using the procedure described in  
7 Example 11 and with catalysts that were not contacted with a  
8 sulfur composition prior to the commencement of the shift re-  
9 action. In the case of the catalyst materials that were not  
10 presulfided prior to use, all of the catalysts were contacted  
11 with some 5 - 10 cc's of water as high temperature steam prior  
12 to contacting a catalyst with the process reagents under shift  
13 reaction conditions.

14         The results of the tests are set forth in the attached  
15 Figure. The relative catalyst activity values depicted in the  
16 Figure were assigned by comparing the reaction rates encountered  
17 with the use of the various catalysts at partial conversion con-  
18 ditions and assuming a first order reaction with respect to car-  
19 bon monoxide conversion.

20         As can be seen in the Figure, a dramatic increase in  
21 the relative activity of the various catalysts was encountered  
22 when the weight ratio of the hydrogenation-dehydrogenation com-  
23 ponent, calculated as a metal oxide, with respect to the alkali  
24 metal component, calculated as oxide, was decreased from a  
25 value of about 10:1, or conversely, when the weight amount of  
26 alkali metal compound on the catalyst was increased relative  
27 to the weight of the base material plus the hydrogenation-de-  
28 hydrogenation component. The Figure also illustrates that the  
29 presence of small amounts of alkali compound (0.6 wt. %  $K_2O$ )  
30 on the catalyst has a negligible effect on catalyst activity.  
31 The data presented clearly demonstrates the critical nature of  
32 the weight ratios of the hydrogenation-dehydrogenation component



1 relative to the alkali metal oxide component of the catalyst.  
2 The Figure also illustrates that presulfiding the non-noble  
3 metal containing shift catalyst prior to use has a substantial  
4 beneficial effect on catalyst performance.

5 EXAMPLE 14

6 A final series of tests were conducted to demonstrate  
7 the suitability of catalysts made up of noble metals in com-  
8 bination with an alkali metal compound for promoting the shift  
9 reaction. In each test a 30 cc catalyst charge was contacted  
10 in the apparatus described in Example 11 with a gas mixture com-  
11 posed of approximately 51 volume % carbon monoxide and 49 volume  
12 % of hydrogen. The gas mixture was introduced into the reactor  
13 at a rate sufficient to maintain an exit dry gas rate at room  
14 temperature of 1.33 liters per minute. This rate corresponds  
15 to 1.21 liters per minute at standard conditions. One cubic  
16 centimeter of water was introduced into the system per minute  
17 as high temperature steam. Both the feed gas and steam were  
18 passed over a zinc oxide bed prior to entry into the reaction  
19 zone to remove any hydrogen sulfide contained in the feed gas.

20 With the exception of the 5 wt. % palladium on alumina  
21 catalyst (a commercially available composition), the noble metal  
22 catalysts were prepared by impregnating the support material  
23 with a sufficient amount of a noble metal salt contained in  
24 water solution to secure the desired amount of noble metal on  
25 the support. Thereafter, the metal containing support material  
26 was calcined in order to convert the water soluble noble metal  
27 salt to the corresponding oxide. Finally, the noble metal-  
28 containing catalyst was impregnated with an aqueous solution  
29 of potassium carbonate and the total system dried at a tempera-  
30 ture varying from 100°- 150°C. Except as indicated, all cata-  
31 lysts contained potassium carbonate in amounts corresponding  
32 to 0.00174 gram atoms of potassium per cubic centimeter of

- 1 base, in the case of non-metal containing catalysts, or base
- 2 plus metal, in the case of noble metal-containing catalysts.
- 3 The results of the tests are set forth in Table XI below.



TABLE XI - (Continued)

	Catalyst		K <sub>2</sub> CO <sub>3</sub> 0.2 wt. % Pd on Activated Carbon	K <sub>2</sub> CO <sub>3</sub> on Activated Carbon	K <sub>2</sub> CO <sub>3</sub> 0.1 wt. % Pt on Low Surface Area Alpha Alumina (a)	K <sub>2</sub> CO <sub>3</sub> 0.1 wt. % Pt on Unrecalcined Alumina High Surface Area
	Wt. Ratio Metal Oxide/Alkali Oxide	Temp. (°F.)				
1						
2						
3						
4						
5						
6						
7			0.014	-	0.014	0.009
8						
9						
10						
11	825	550				
12	725	550				
13	700	550		43.3		
14	625	550				
15	600	550	34.8	6.5		
16	575	550				
17	525	550	8.6		78.0	17.9
18	525	200			35.5	
19	425	550				
20	425	200			7.2	
21	350	0				
22	(a) No calcination after platinum impregnation.					

As can be seen by referring to Table XI, the noble metal based compositions possess significant catalytic activity for promoting the shift reaction. High activity is shown when a given catalyst serves to convert significant amounts of the CO in the gas stream at relatively mild temperature and pressure conditions.

#### EXAMPLE 15

A catalyst was prepared similar to that of Example 10 except that  $8.7 \times 10^{-4}$  moles of sodium carbonate per cubic centimeter of base plus cobalt oxide and molybdenum oxide was used instead of potassium carbonate. The catalyst was presulfided prior to use following the procedure of Example 11 and was subsequently used, following the procedure of Example 10, to treat, under shift conditions, a reagent stream containing 50.68 volume % hydrogen, 48.97 volume % carbon monoxide, 0.02 volume % carbon dioxide and 1.04 volume % hydrogen sulfide. The effluent from the shift reactor was analyzed for carbon monoxide content to determine the activity of the catalyst. The results of the tests are set forth in Table XII.

TABLE XII

	Temperature (°F.)	Pressure (psig)	Volume % CO contained in dry product gas	% CO Conversion
24	625	550	1.23	96.4
25	525	550	0.50	98.5
26	425	200	0.20	99.4
27	350	100	14.12	62.2

The above data clearly demonstrate that sodium compounds, in particular, sodium carbonate, is a highly effective shift catalyst component.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. A process for the conversion of carbon monoxide and steam to hydrogen and carbon dioxide which comprises contacting said carbon monoxide and steam under shift reaction conditions with a catalyst comprising: (i) an alkali metal compound derived from an acid having an ionization constant less than  $1 \times 10^{-3}$  and (ii) a hydrogenation-dehydrogenation component selected from the group consisting of ruthenium, palladium, osmium, iridium, platinum, and mixtures thereof, the weight ratio of said hydrogenation-dehydrogenation component, calculated on the basis of the oxide thereof, to said alkali metal compound, calculated on the basis of the oxide thereof, being in the range of from about 0.001:1 to about 10:1.
2. The process of claim 1 wherein said alkali metal compound is an alkali metal carbonate.
3. The process for the conversion of gas mixtures containing carbon monoxide and steam and being substantially free of a sulfur material to hydrogen and carbon dioxide which comprises contacting said gas mixture substantially in the vapor phase and under shift reaction conditions with a catalyst comprising: (i) an alkali metal compound derived from an acid having an ionization constant less than  $1 \times 10^{-3}$ , and (ii) a hydrogenation-dehydrogenation component comprising a noble metal of Group VIII of the Periodic Table and mixtures thereof, the weight ratio of said noble metal hydrogenation-dehydrogenation component, calculated on the basis of the oxide thereof, to said alkali metal compound, calculated on the basis of the oxide thereof, being in the range of about 0.0001:1 to about 10:1.
4. The process of claim 3 wherein said catalyst is contained on a support material.

5. The process of claim 3 wherein said alkali metal compound is an alkali metal carbonate.
6. The process of claim 4 wherein said alkali metal compound is potassium carbonate.
7. The process of claim 6 wherein said support is alumina.
8. An improved catalyst composition comprising, in combination, (i) an alkali metal compound derived from an acid having an ionization constant less than  $1 \times 10^{-3}$  and (ii) a hydrogenation-dehydrogenation component comprising a noble metal constituent selected from the group consisting of ruthenium, palladium, osmium, iridium, platinum, and mixtures thereof, the weight ratio of said hydrogenation-dehydrogenation component, calculated on the basis of the oxide thereof, to said alkali metal compound, calculated on the basis of the oxide thereof, being in the range of from about 0.0001:1 to 10:1.
9. The catalyst compositions of claim 8 contained on a support material.
10. The catalyst composition of claim 9 wherein the support is alumina.
11. The composition of claim 8 wherein said alkali metal compound is an alkali metal carbonate.
12. The composition of claim 9 wherein said alkali metal compound is potassium carbonate.
13. A process for the conversion of carbon monoxide and steam to hydrogen and carbon dioxide which comprises contacting said carbon monoxide and steam under shift reaction conditions with a catalyst comprising: (i) an alkali metal compound derived from an acid having an ionization constant less than

$1 \times 10^{-3}$  and (ii) a hydrogenation-dehydrogenation component comprising a noble metal constituent selected from the group consisting of ruthenium, palladium, osmium, iridium, platinum, and mixtures thereof, the weight ratio of said hydrogenation-dehydrogenation component, calculated on the basis of the oxide thereof, to said alkali metal compound, calculated on the basis of the oxide thereof, being in the range of from about 0.0001:1 to about 10:1.

14. The process of claim 13 wherein said alkali metal compound is an alkali metal carbonate.

15. The process of claim 14 wherein said alkali metal carbonate is potassium carbonate.

16. The process of claim 13 wherein said catalyst is contained on a support material.

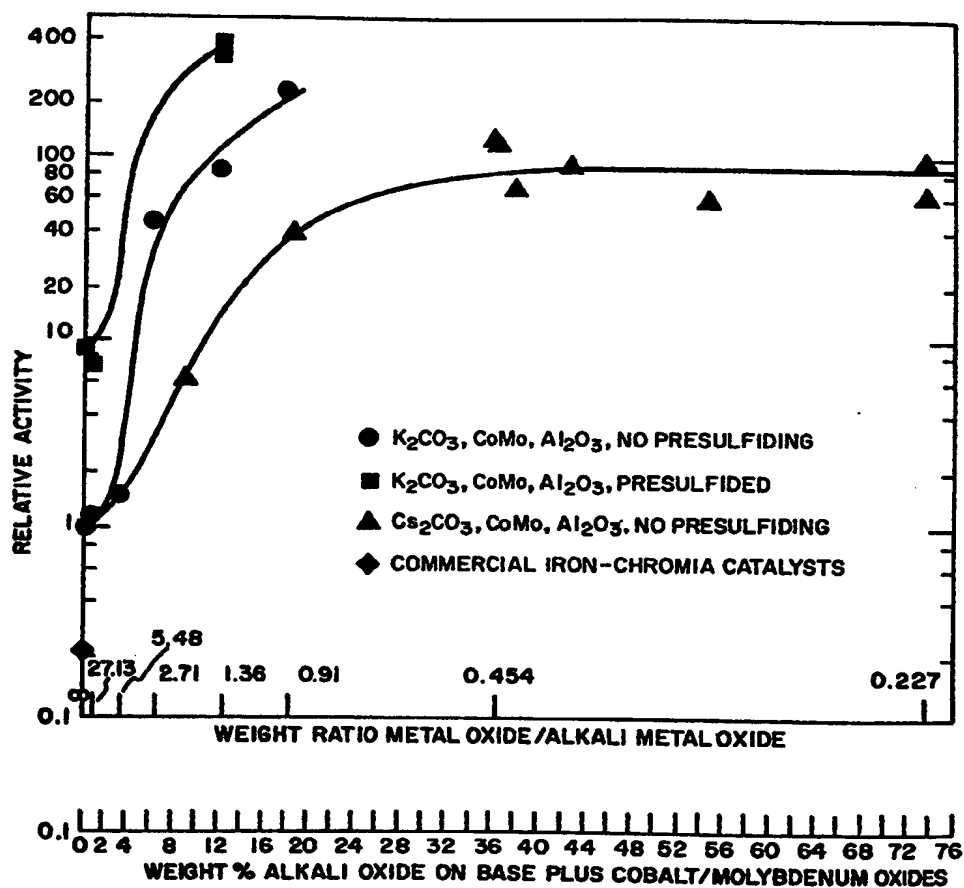
17. The process of claim 16 wherein said support is alumina.

18. The process of claim 13 wherein said process is conducted at a temperature in the range of 300 to 700°F.

19. The process of claim 13 wherein said process is conducted at a pressure varying from about 200 to 3000 psig and at a space velocity of at least 300 volumes of gas mixture per volume of supported catalyst per hour.







PATENT AGENTS